SYNTHESIS, MICROWAVE SPECTRA, X-RAY STRUCTURE AND HIGH-LEVEL CALCULATIONS FOR FORMAMIDINIUM FORMATE

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An efficient synthesis of formamidinium formate is described. The experimental x-ray structure shows both internal and external H-bonding to surrounding molecules. However, in the gas phase, this compound occurs as a doubly hydrogen bonded dimer. This doubly hydrogen-bonded structure is quite different from the solid state structure. Microwave spectra were measured in the 6-14 GHz range using a pulsed-beam Fourier transform microwave (MW) spectrometer. The two nonequivalent N-atoms exhibit distinct quadrupole coupling. The rotational, centrifugal distortion, and quadrupole coupling constants determined from the spectra have the following values: A=5880.05(2), B=2148.7710(2), C=1575.23473(13), 1.5χaa (N1)=1.715(3), 0.5(χbb-χcc) (N1)=-1.333(4), 1.5χaa (N2)=0.381(2), 0.5(χbb-χcc) (N2)= -0.0342(2), and D_J=0.002145(5) MHz. The experimental inertial defect, Δ=-0.243amu Å^2, is consistent with a planar structure. Accurate and precise rotational constants (A, B and C), obtained from the MW measurements, were closely reproduced, within 1%-2% of the measured values, with the M11 DFT functional theoretical calculations. Detailed comparison of the measured and calculated A, B, and C rotational constants confirms the planar doubly hydrogen bonded structure. The calculated nitrogen quadrupole coupling strengths of the monomer are quite different from either of the two nitrogen sites of the dimer. The poor agreement between measured and calculated quadrupole coupling strengths shows that the dimer is not locked in the equilibrium structure but is likely undergoing large amplitude vibrational motion of the hydrogen atoms moving between the N and O atoms involved in the hydrogen bonding.